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With international search report.

(54) Title: PROCESS FOR THE PREPARATION OF A GRAFT COPOLYMER BOUND CATALYST

(57) Abstract

The object of the present invention is a process of preparation of a graft copolymer obtained by pre-irradiation grafting of vinyl monomers onto polyolefins or fluorinated polyethylenes, in particular, of grafting acrylic or methacrylic acid onto polyethylene and/or polypropylene and subsequently loading a metal, such as a transition metal on the graft copolymer obtained. Such metal-loaded graft copolymers find use, especially as catalysts, e.g. for hydrogenation reactions.

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PROCESS FOR THE PREPARATION OF A GRAFT COPOLYMER BOUND CATALYST

FIELD OF INVENTION

This invention relates to a process of preparing a metal loaded graft copolymer, in particular a copolymer bound transition metal catalyst that is very easy to separate from the reaction solution, and which is non-pyrophoric and reusable. It is especially suitable for use in continous flow processes. The invention also relates to the said graft copolymer bound catalyst obtainable by the said process, as well as to its use e.g. in hydrogenation reactions.

BACKGROUND OF THE INVENTION

The idea of anchoring transition metal catalysts to organic polymers has interested scientists, such studies having sought to produce heterogenized catalyst systems while having the distinguishing characteristic of being easily separable from the reaction media (Hodge, P., Sherrington, D. C. (Eds.), *Synthesis and separations using functional polymers*, John Wiley & Sons, New York, (1988)).

Polymer-bound transition metal catalysts may offer a number of advantages, such as

- greater catalytic activity, due to lack of formation of ligand-bridged complexes as one catalytic site may be isolated from another,
- two active catalysts anchored to the same polymer backbone can in some cases be used to conduct sequential multistep organic synthesis,
- minimized losses during use of polymeric catalysts,
- increase of substrate selectivity due to an increase in the steric environment.

Further, the selectivity of the polymer towards different substrates can be controlled by the loading of the catalyst on the polymer support, controlling the degree of resin swelling and introducing optically active groups in the polymer around the active site.

A polymer support used in a particular application should fulfill a number of important functions simultaneously. First, the support must possess the correct mechanical properties. For example, in column or batch applications, resin beads must be mechanically strong to resist compression and fractional friction. Secondly, the support must possess the correct physical structure in order to ensure that a high amount of the functional groups in the material are accessible to the reaction phase. Finally, the support must provide the correct microenvironment to optimize the process being carried out, e.g. it must provide the correct polarity, hydrophilicity, microviscosity etc. In general, these support requirements have been demanded by default rather than by careful argument and design. When looking at the traditional styrene divinylbenzene resins it seems clear that the desirable features, especially in the accessibility-capacity relation, tend to be mutually exclusive and that for any particular application a compromise has to be made *(Guyot, A., Reactive Polymers.* _16_ *(1992), 233)*.

Further, since polymer supported catalysts are more expensive than their homogeneous analogues, it is vital that they can be recycled.

A useful method for preparing polymer bound reactants, with a potential of solving many of the problems mentioned above, is grafting and especially radiation grafting offers promising new opportunities (Hartley, F. R., *J. Polym. Sci., Polym. Chem. Ed.,* _20_, (1982), 2395; Garnett, J. L.,

J. Polym. Sci., Polym. Lett., 19, (1981), 23; Akelah, A., *J. Appl. Polym. Sci.*, 28, (1983), 3137). This method involves taking a polymer with appropriate morphology and physical properties and introducing reactive sites, free radicals, into the polymer chain by irradiation. The free radicals can either combine to give cross-links, as is the case for example polyethylene, or cause chain scission, as is the case for polypropylene. In the presence of vinyl monomers, on the other hand, the free radicals can initiate graft copolymerization.

The preparation of graft copolymers and the use of graft copolymers in a variety of applications are well known both in literature and patents (Stannet, V. et. al., *Radiat. Phys. Chem.*, 35, (1990)).

Three different methods of radiation grafting have been developed and most of the work done has concentrated on the use of low dose rate gamma rays from ^{60}Co sources. During the past few years, however, there has been much interest in using high energy electrons from accelerators with high dose rates (10^6 - 10^9 rads/sec), since these high dose rates make radiation chemical processes commercially more attractive. The chemistry involved is, however, similar whether gamma or electron radiation is utilized, and therefore the graft result using the different sources does not significantly differ. The three methods of radiation grafting that have received special attention are: (1) direct radiation grafting of a vinyl monomer onto a polymer (*mutual grafting*), (2) grafting on radiation-peroxidized polymers (*peroxide grafting*) and (3) grafting initiated by trapped radicals (*pre-irradiation grafting*).

The mutual grafting by irradiating the polymer in the presence of the monomer is a fairly simple and effective method, since the free radicals initiate polymerization immediately as they are generated. The disadvantage of

this method is, however, that simultaneously with the graft copolymerization, homopolymerization of the monomer occurs upon irradiation.

When grafting on radiation-peroxidized polymers the polymer is first irradiated in the presence of oxygen, thus forming peroxides and hydroperoxides that are stable and can be stored in the polymer for a long period of time. Grafting is activated by cleavage of the peroxides or hydroperoxides by heat, UV-light or catalysts in a monomer solution.

The pre-irradiation grafting by irradiation of the polymer alone in an inert atmosphere and immersing the irradiated polymer in a monomer solution requires additional steps in comparison to direct grafting, but the advantage is that only a small amount of homopolymer is formed, mainly by a chain transfer process. The grafting process is controlled by the diffusion of the monomer in the polymer and can to some extent be facilitated by the use of solvents that are able to swell the formed graft copolymer.

Pre-irradiation grafting is mostly preferred since this method produces only small amounts of homopolymer in comparison to mutual grafting.

SUMMARY OF THE INVENTION

The object of the present invention is a process of preparation of a graft copolymer obtained by pre-irradiation grafting of vinyl monomers onto polymers, in particular, onto polyolefins, and subsequently loading a metal, such as a transition metal on the graft copolymer obtained. Such metal-loaded graft copolymers find use especially as catalysts, e.g. for hydrogenation reactions.

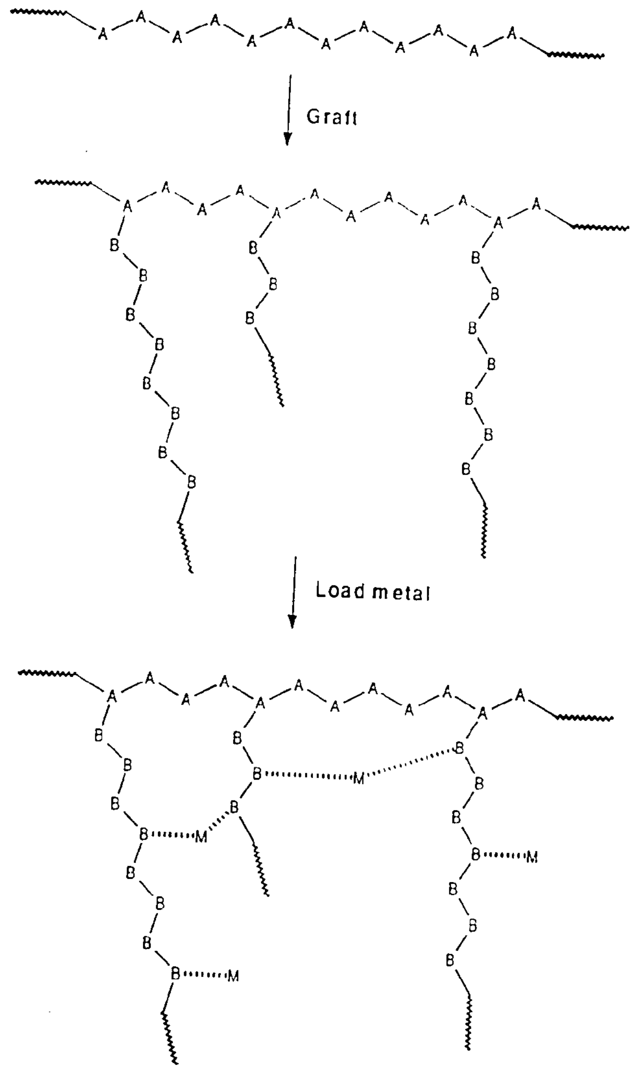
DETAILED DESCRIPTION OF THE INVENTION

More specifically the invention relates to a process which comprises the steps of

- exposing an organic polymer selected from the group of polyolefins and fluorinated polyethylenes to radiation in an inert atmosphere,
- immersing the irradiated polymer in an aqueous solution of a monomer selected from the group of acrylic acid, methacrylic acid and a mixture thereof,
- separating the resulting graft copolymer, and
- loading a metal onto the graft copolymer.

The polymers grafted according to the invention exhibit many feasible properties, such as having non-crosslinked grafted side chains, a polymer support which is chemically inert and mechanically rigid, the possibility of achieving a very high capacity, i.e. a high extent of grafting, as well as a high accessibility if the grafted copolymer is allowed to swell in a suitable solvent. The graft copolymers obtained usually combine both excellent chemical resistance and mechanical strength, and a great advantage is that a polymer sample in any form of a film, fiber, pellets, hollow fiber, membrane or non-woven can be graft modified. Surprisingly the metal loaded graft copolymer can be recycled and reused in several subsequent hydrogenation reactions and is non-leaching, which latter characteristic has been major problem with previous known catalysts (*Hodge, P., Sherrington,* supra p. 134, 135 and 138).

The process according to the invention is illustrated in the following reaction scheme outlining the steps of grafting and subsequently loading with a metal.



When the organic polymer is a polyolefin, A is $-CH_2-CHR-$ wherein R is H or $(CH_2)_nCH_3$, wherein n is 0 to 20, or, when the organic polymer is a fluorinated polyethylene, A preferably has the meaning of $-CF_2-CX_2-$ wherein each X is H or F, B is $-CH_2-CR_1(COOH)-$ wherein R_1 is H or CH_3, and M is a metal, preferably Pd or Ru. The weight ratio B/A is from 0.5 to 20, preferably 1 to 6, and the mole ratio M/B is from 0.001 to 0.5, preferably 0.01 to 0.1.

The polyolefins used are thus polymers formed from α-olefins. According to a preferred embodiment, the α-olefins used contain up to 8 carbon atoms (n=6). Particularly

preferred polyolefins are homo- and copolymers of ethylene or propylene. The fluorinated polyethylene backbone is preferably polyvinylidene fluoride or polytetrafluorethylene, i.e. Teflon.

The process according to the invention thus comprises a first step of irradiating the polymer sample with electrons (or any other form of ionizing radiation) from an accelerator under an inert atmosphere (<300 ppm 0_2) using a radiation dose dependent on the sample treated. The irradiated specimens are then immersed in acrylic or methacrylic acid/water solutions at selected temperatures, and graft copolymer samples, modified with different amounts of polyacrylic/polymethacrylic acid, can be prepared by varying the reaction time and the concentration of monomer in the graft solution. The concentration of monomer in the graft solution can vary widely, typically it is from e.g 10 to 70 % by volume, at which concentration an extent of grafting suitable for most purposes can be achieved. For the purpose of the invention an extent of grafting of appr. 50 to 2000 %, preferably 100 to 600 % is suitable. Under typical manufacturing conditions such a preferred concentration is normally reached by using a concentration of monomer of appr. 10 to 50 % by volume.

It is necessary to remove in advance any dissolved oxygen from the aqueous solution of the monomer by purging the solutions with nitrogen, since oxygen readily inhibits the progress of the graft reaction. It may also be effective to add Mohr's salt to inhibit the formation of acrylic/methacrylic acid homopolymer during the grafting. The resulting graft copolymers are e.g. Soxhlet extracted with water overnight to remove unreacted monomer and homopolymer. The grafted samples are then usually dried to constant weight, prior to loading, e.g. in an oven. The extent of grafting is determined according to

$$\frac{(m_1 - m_0)^* 100}{m_0} = \text{extent of grafting (\%)}$$

m_0 = weight of the original sample
m_1 = weight of the grafted sample

The temperature of the graft solution can be varied in the range of 20 - 80°C, but the graft reaction is more easily controlled in the temperature range of 20 - 50°C.

After grafting, metal ions, preferably transition metal ions, are loaded onto the graft copolymer e.g. in an ion - exchange reaction. If the graft copolymer is dried after the grafting step, the graft copolymer is swollen prior to loading with the metal, advantageously by keeping it in a suitable solvent, such as water, overnight in order to achieve maximum swelling. A water solution of e.g. a suitable transition metal salt, such as a chloride, is added and the mixture is stirred e.g. for 48 h. The resulting metal loaded graft copolymer is extracted, such as Soxhlet extracted, with water e.g. for 24 h to remove any unbound ions, and dried.

The amount of metal in the polymer can be determined e.g. by repeated extraction with 1 M hydrochloric acid followed by direct current plasma emission spectroscopy (DCP) analysis of the extract.

The invention is explained more in detail by the following examples, but it should be noted that the invention is not to be limited by these examples.

<u>Example 1</u>

Grafting of acrylic acid onto polypropylene film.

Polypropylene 50 µm thick films were irradiated under a nitrogen atmosphere using an Electrocurtain® electron

accelerator, operating at 175 kV, to a total dose of 50 kGy. The irradiated films were immediately immersed in aqueous solutions of acrylic acid, which were purged with nitrogen in advance for at least 30 minutes. The temperature of the graft solution was 70°C. Different graft copolymers were obtained by varying the amount of acrylic acid in the graft solution and the reaction time. When the reactions were terminated the grafted films were Soxhlet extracted with water overnight and the extent of grafting was calculated as described above. The extent of grafting as a function of reaction time and concentration of acrylic acid in the graft solution is presented in Figure 1.

Example 2

Grafting of acrylic acid onto polypropylene fibers.

Chopped polypropylene fibers (12 mm long) were placed in a sealable plastic bag and the bag was purged with nitrogen for at least 60 minutes and closed. The bag was irradiated with 10 MeV electrons from a linear accelerator (EB 10, Scanditronix) to a total dose of 25 kGy. The fibers were removed from the bag and immediately immersed in a nitrogen purged aqueous solution containing 50 vol % acrylic acid for 30 minutes at 70°C. The grafted fibers were Soxhlet extracted with water overnight, dried to constant weight and the extent of grafting was calculated to 250 %.

Example 3

Grafting of acrylic acid onto polypropylene non-woven.

A polypropylene non-woven fabric was irradiated under a nitrogen atmosphere using an Electrocurtain® electron accelerator, operating at 175 kV, to a total dose of 500 kGy. The fabric was immediately immersed in a nitrogen purged aqueous solution containing 30 vol % acrylic acid for 4 hours at 40°C. The grafted fabric was Soxhlet extracted overnight and the extent of grafting was calculated to

630 %.

Example 4

Preparation of a polymer supported palladium catalyst.

10 g of a polyacrylic acid grafted polypropylene fiber, prepared as outlined in Example 2, was allowed to swell in distilled water overnight. To the swollen fibers 0.78 g $PdCl_2$ was added in large amount of distilled water. The fibers turned brown almost immediately. The mixture was stirred for 48 h or until a completely clear solution was obtained. After this the palladium loaded polymer was separated, rinsed with water, Soxhlet extracted with water for 24h and finally dried. The amount of palladium in the fiber was determined by repeated extraction with 1 M hydrochloric acid followed by DCP analysis of the extract. The amount of palladium was found to be 0.44 mmol Pd/g fiber.

Example 5

Preparation of a non-woven fabric supported palladium catalyst.

1 g of a non-woven fabric prepared as in Example 3 was allowed to swell in distilled water overnight. To the swollen non-woven was added 0.16 g $PdCl_2$ in distilled water. The mixture was stirred for 48 h. After this the palladium loaded fabric was separated, rinsed with water, Soxhlet extracted with water for 24 h and finally dried. The amount of palladium in the fabric was determined by repeated extraction with 1 M hydrochloric acid followed by DCP analysis of the extract. The amount of palladium was found to be 0.91 mmol Pd/g fiber.

Example 6

Preparation of a polymer supported ruthenium catalyst.

1 g of a non-woven fabric prepared as in Example 3 was allowed to swell in distilled water overnight. To the swollen fabric was added 0.48 g $RuCl_4$ in distilled water. The mixture was stirred for 48 h. After this the ruthenium loaded fabric was separated, rinsed with water, soxhlet extracted with water for 24 h and finally dried.

Example 7

Hydrogenation of 1-octene catalyzed by palladium loaded polypropylene-graft-poly(acrylic acid) fibers.

Before use the palladium loaded polymer, made according to the Example 4 and containing 0.44 mmol Pd/gram fiber, was treated with hydrogen in order to reduce palladium (II) to palladium (0), by suspending it in methanol and passing hydrogen gas through for two hours.

The hydrogenations of 1-octene were carried out in a 100 ml round-bottomed flask. The vessel was thermostated to 30°C, provided with a magnetic stirrer and connected to a gas burette that maintained the reaction at constant 1 atm. hydrogen pressure. In the reaction vessel 0.12 g of the dried palladium catalyst and 45 ml of methanol were placed. Stirring was started and the air in the system was displaced by repeating the process of evacuating and flushing with hydrogen three times. Finally, an adequate amount of hydrogen gas was stored in the gas burette, and the mixture was stirred 30 minutes to saturate the solution with hydrogen. The stirring was stopped and 5 ml of a 0.995 M 1-octene solution in methanol was injected into the reaction vessel. The reaction was initiated by starting the stirrer. The stirring was 1000 rpm. The progress of the hydrogenation was followed by recording the hydrogen uptake vs. time. The initial rates of the hydrogenations were calculated

from the slope of the amount of hydrogen absorbed versus the reaction time. The catalyst was easily recovered by decanting the reacting mixture and was reused after washing with methanol. The reaction rates and the catalytic activity varied very little over ten runs. The calculated rates can be seen in Figure 2. A mean value for the half lifes found during the ten hydrogenation cycles was 25 minutes.

No palladium could be detected with direct current plasma emission spectroscopy (DCP) analysis of the reaction solutions after the catalyst was removed.

Example 8

Hydrogenation of 1-octene catalyzed by palladium loaded polypropylene-graft-poly(acrylic acid) non-woven fabric.

Before use the palladium loaded fabric, prepared according to Example 5, was treated with hydrogen in order to reduce palladium (II) to palladium (0), by suspending it in methanol and passing hydrogen gas through for two hours.

0.12 gram of the polymer bound catalyst was used for the hydrogenation of 1-octene. The hydrogenations were carried out in accordance with Example 7. The catalyst was easily recovered by picking up the fabric from the reaction solution and was reused after washing with methanol. The catalyst was reused several times with similar reaction kinetics. The half life of the hydrogenation reaction was found to be 10 minutes. The reaction rate was found to be 0.2 ml H_2/sgPd.

Claims

1. Process for the preparation of a metal loaded graft copolymer comprising the steps of

- exposing an organic polymer selected from the group of polyolefins and fluorinated polyethylenes to radiation in an inert atmosphere,
- immersing the irradiated polymer in an aqueous solution of a monomer selected from the group of acrylic acid, methacrylic acid and mixtures thereof,
- separating the resulting graft copolymer, and
- loading a metal onto the graft copolymer.

2. Process according to claim 1, wherein the polyolefin is a polymer of an α-olefin of up to 8 carbon atoms.

3. Process according to claim 2 wherein the polyolefin is selected from the group consisting of propylene and ethylene homopolymers and copolymers thereof.

4. Process according to claim 1, wherein the graft monomer is acrylic acid and the polyolefin is polypropylene.

5. Process according to claim 1, wherein the fluorinated polyethylene is selected from polyvinylidene fluoride and polytetrafluorethylene.

6. Process according to claim 4, wherein the metal to be loaded is a transition metal, selected from the group consisting of palladium and ruthenium.

7. Process according to claim 1, wherein the polymer is in the form of a fiber, hollow fiber, pellet, membrane, film, or a non-woven fabric.

8. Metal loaded graft copolymer comprising a polymer backbone selected from the group of polyolefins and fluo-

rinated polyethylenes grafted with acrylic and/or methacrylic acid, the weight ratio between grafted monomer and polymer backbone being from 0.5 to 20, and the mole ratio between loaded metal and grafted monomer being from 0.001 to 0.5.

9. Metal loaded graft copolymer according to claim 8, wherein the weight ratio between grafted monomer and polymer backbone is 1 to 6, and the mole ratio between loaded metal and grafted monomer is 0.01 to 0.1.

10. Metal loaded graft copolymer according to claim 8 or 9, wherein the organic polymer is a polyolefin selected from the group consisting of polypropylene, polyethylene and mixtures thereof.

11. Metal loaded graft copolymer according to claim 8 or 9, wherein the polyolefin is polypropylene, grafted with acrylic acid and loaded with a transition metal.

12. Metal loaded graft copolymer according to claim 8 or 9, wherein the polyolefin is polypropylene, grafted with acrylic acid and loaded with a transition metal selected from the group of palladium and ruthenium.

13. Metal loaded graft copolymer according to claim 8 wherein the polymer is in the form of a fiber, hollow fiber, pellet, membrane, film, or a non-woven fabric.

14. Metal loaded graft copolymer according to claim 8, wherein the fluorinated polyethylene is selected from the group of polyvinylidene fluoride or polytetrafluorethylene.

15. Metal loaded graft copolymer comprising a polymer backbone selected from the group of polyolefins and fluorinated polyethylenes grafted with acrylic and/or methacrylic acid, the weight ratio between grafted monomer and

polymer backbone being from 0.5 to 20, and the mole ratio between loaded metal and grafted monomer being from 0.001 to 0.5, the copolymer being obtainable by

- exposing the said organic polymer to radiation in an inert atmosphere,
- immersing the irradiated polymer in an aqueous solution of the monomer selected from the group of acrylic acid, methacrylic acid and mixtures thereof,
- separating the resulting graft copolymer, and
- loading a metal onto the graft copolymer.

16. Metal loaded graft copolymer according to claim 15, wherein the weight ratio between grafted monomer and polymer backbone is 1 to 6, and the mole ratio between loaded metal and grafted monomer is 0.01 to 0.1.

17. Metal loaded graft copolymer according to claim 15 or 15, wherein the organic polymer is a polyolefin selected from the group consisting of polypropylene, polyethylene and mixtures thereof.

18. Metal loaded graft copolymer according to claim 15 or 16, wherein the polyolefin is polypropylene, grafted with acrylic acid and loaded with a transition metal.

19. Metal loaded graft copolymer according to claim 15 or 16, wherein the polyolefin is polypropylene, grafted with acrylic acid and loaded with a transition metal selected from the group of palladium and ruthenium.

20. Metal loaded graft copolymer according to claim 15 or 16, wherein the polymer is in the form of a fiber, hollow fiber, pellet, membrane, film, or a non-woven fabric.

21. Use of a graft copolymer according to claim 8 or 15, wherein the polyolefin is polypropylene, grafted with acrylic acid and loaded with a metal selected from the

group consisting of palladium and ruthenium, as a recyclable hydrogenation catalyst.

22. Method of hydrogenation, wherein as the hydrogenation catalyst, a metal loaded graft copolymer is used comprising a polypropylene backbone grafted with acrylic acid and loaded with a metal selected from the group consisting of palladium and ruthenium.

Fig. 1

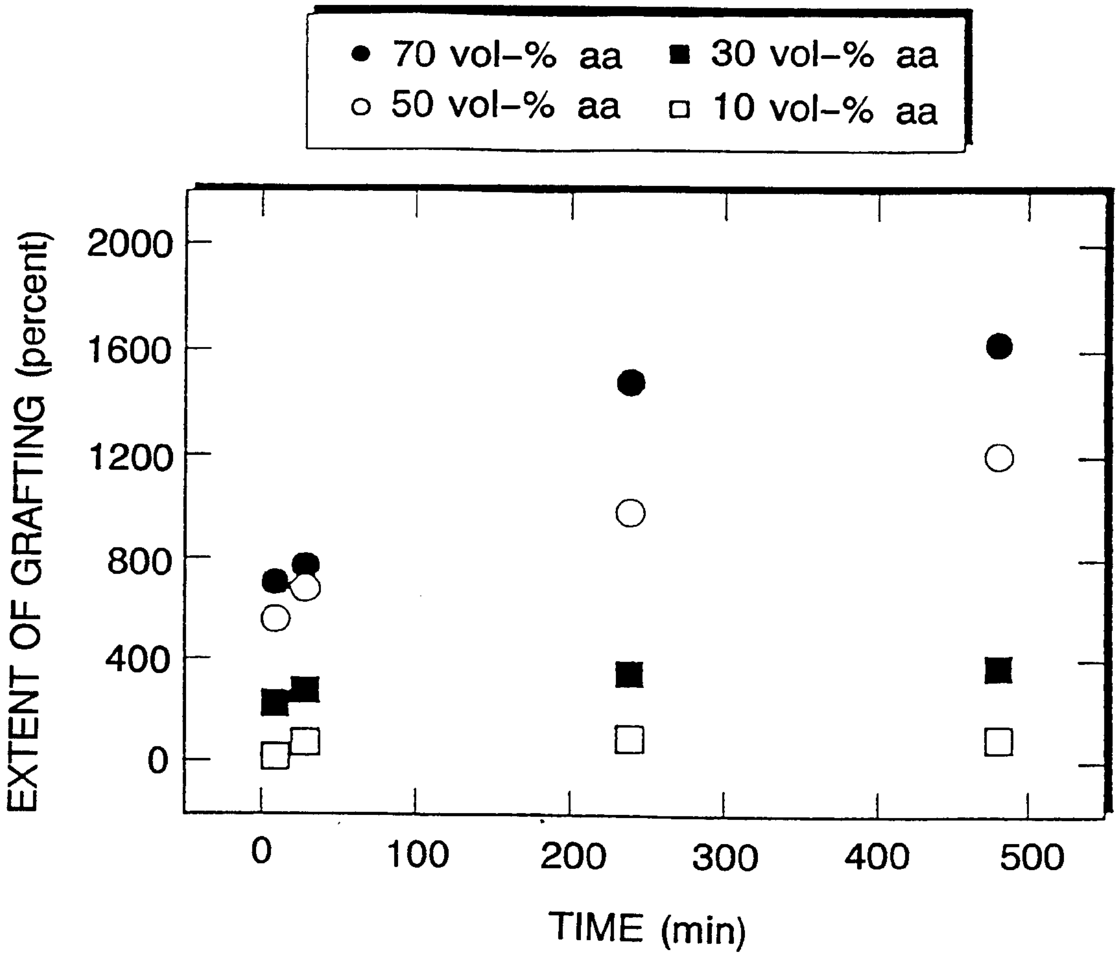
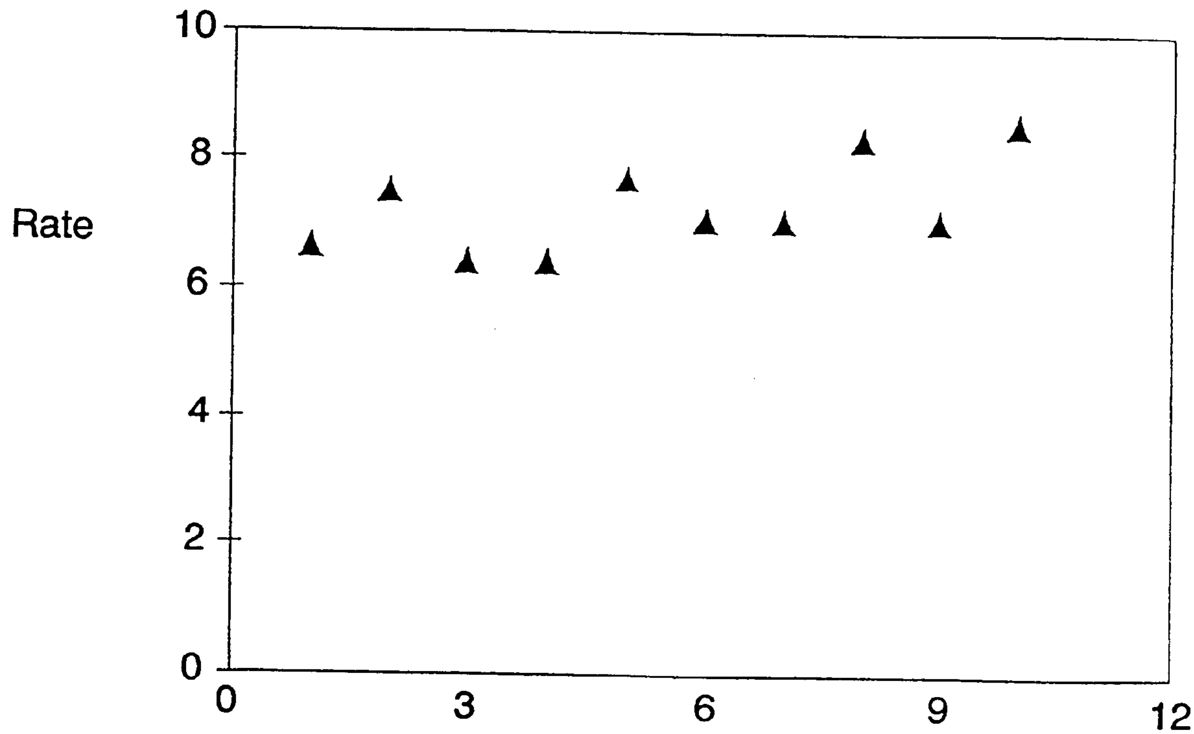

● 70 vol-% aa
■ 30 vol-% aa
○ 50 vol-% aa
□ 10 vol-% aa
EXTENT OF GRAFTING (percent)
2000
1600
1200
800
400
0
0
100
200
300
400
500
TIME (min)

Fig. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 93/00493

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C08F 8/42, B01J 31/06
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: B01J, C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CLAIMS, EPODOC, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A1, 0037953 (VARTA BATTERIE AKTIENGESELLSCHAFT), 21 October 1981 (21.10.81) --	1-22
A	EP, A1, 0008407 (HEYL & CO., CHEM.-PHARM. FABRIK), 5 March 1980 (05.03.80) --	1-22
A	Derwent's abstract, No 47333 D/26, week 8126, ABSTRACT OF SU, A1, 770523 (ZELINSKII ORG CHEM INST(UYSY)), 15 October 1980 (15.10.80) --	1-22
A	Patent Abstracts of Japan, Vol 10,No 185, C-357, abstract of JP, A, 61-33237 (AGENCY OF IND SCIENCE & TECHNOL), 17 February 1986 (17.02.86) --	1-22

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 February 1994	28 -02- 1994
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Barbro Nilsson Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 93/00493

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5128297 (K. TAKAHASHI ET AL.), 7 July 1992 (07.07.92)	1-22

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI93/00493

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 22
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 22 "Method of hydrogenation...." is not clear and concise and therefore does not comply with PCT article 6. As the claim does not adhere to any previous claim it is not clear if it concerns the same inventive concept as those claims. The search has been performed as if claim 22 had refered to a previous claim.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

28/01/94

International application No.
PCT/FI 93/00493

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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